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An Experimental Investigation of Radiation Effects in Semiconductors

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Introduction

The influence of radiation upon the properties of many semiconducting devices depends upon such factors as the concentration of both accidental and intentionally introduced impurities in the material, the nature of the radiation and the temperature of the material following the irradiation. Work has continued during the past six months on a variety of these problems. A comprehensive investigation of the influence of Co^{60} gamma ray irradiation upon the minority carrier lifetime of silicon has been reported in the Ph.D. thesis of Dr. Ralph Hewes. Additional data have been obtained on the recombination luminescence of silicon that has been irradiated with Co^{60} gamma rays and fast neutrons. This work is expected to be completed and will be reported in detail in a Ph.D. thesis before the next reporting date for this grant. Initial success utilizing a tunneling junction of semiconductor-insulator-superconductor has demonstrated the feasibility of utilizing this technique for determining the fundamental properties of highly doped semiconductors. The study of the thermal stability of defects introduced into highly doped germanium by fast neutron irradiation was completed during this reporting period.

Recombination Luminescence

Studies of the recombination luminescence of optically excited carriers have been extended to liquid helium temperatures with a consequent increase in the resolution of the emission bands. Measurements have been made on n- and p-type Czochralski grown silicon that have been irradiated with 1×10^8 roentgens of Co^{60} gamma rays.

Results for n- and p-type float zone grown material are similar and typical data for the n-type are shown in Figures 1-3. There are four main bands centered at 1.280, 1.301, 1.342, and 1.380 microns, corresponding to photons with energies of 0.969, 0.953, 0.924, and 0.897 eV.

The widths of the first and fourth bands suggest that they arise from transitions between bound states and do not involve the emission of phonons. The states are probably those of an electron and a hole localized at the silicon A-center. Using the value 1.165 eV for the energy gap and assuming that the electron is in its ground state, 0.17 eV below the conduction band, the hole states are found to be 0.026 eV and 0.096 eV above the valence band. These energies agree reasonably well with the theoretical model of Kurskii[1] who obtained .021 eV and .134 eV for the first excited and ground states of the trapped hole.

The second band at 0.953 eV is probably due to recombination between the electron in the ground state of the A-center and free holes, with the emission of a transverse acoustic phonon having an energy of 0.049 eV. The third band at 0.924 eV seems to have several components which have not been resolved and could possibly be due to recombination with free holes with muitiple phonon emission. The three highest energy bands have been observed by Yukhnevich[2] at 80°K using electrical injection in Czochralski silicon. He has not reported an observation of the 1.380 micron band.

The luminescence spectrum of n-type Czochralski silicon is the same as float zone silicon except that there is a sharp isolated band located at 1.568 microns corresponding to a photon with an energy of 0.791 eV. This band is similar in intensity and halfwidth to the 1.380

micron band and would seem to be associated with the presence of oxygen ($\sim 10^{18}/cm^3$) found in Czochralski grown material. It also probably originates from phononless transitions between localized electron and hole states of the center. In p-type Czochralski silicon, an additional complicated band occurs between 1.45 and 1.9 microns as shown in Figure 4. The nature of this band is not yet understood.

The luminescence observed by Yukhnevich and Tkachev[3] between 3.00 and 2.40 at 80°K has not been observed in any samples at helium temperatures.

It should be noted that the same luminescence occurs between 1.28 microns and 1.40 microns in all materials, strongly suggesting that the same defects are produced in all of the materials by the radiation. Additional luminescence at longer wavelengths in the pulled material suggests other defects that may be associated with oxygen.

Measurements will be continued on neutron irradiated material at helium temperature. Data have already been taken at liquid nitrogen temperature on these samples. Samples having different degrees of chemical doping will also be investigated.

Minority Carrier Lifetimes in Irradiated Materials

The Shockley-Read theory predicts that for centers which act as recombination sites and are effectively always empty the lifetime for holes τ_{p_o} will be given by

$$1/\tau_{p_o} = N\sigma_p v_p$$

where N is the concentration of the recombination centers, σ_p is the cross-section for trapping holes, and v_p is the thermal velocity of the holes. In earlier work,[4] the low temperature lifetime-flux product $\tau_{p_o}\Phi$ was determined for the deep recombination level at E_c - 0.4 eV in n-type material. For a gamma ray flux Φ,

$$1/\tau_{p_o}\Phi = \frac{N}{\Phi}\sigma_p v_p$$

Current investigations are underway to determine (N/Φ) by Hall measurements. This will allow, therefore, the cross-section for hole trapping to be determined from

$$\sigma_p = \left(\frac{1}{\tau_{p_o}\Phi}\right)_{\text{Lifetime}} \left(\frac{\Phi}{N}\right)_{\text{Hall}} \frac{1}{v_p}$$

Further studies are being made of the annealing of the recombination centers previously observed in both n- and p-type materials. Photoconductivity studies are also being carried out in an effort to observe the traps that are present both before and after gamma ray irradiation. The material presented in the thesis of R. Hewes is being prepared for publication.

Tunneling Between a Semiconductor and Superconductor

The value of electron tunneling measurements in studying the electron density of states in semimetals and near-degenerate semiconductors respectively has been demonstrated by the work of Esaki[5] and Gray.[6] These workers have shown that the differential conductance di/dV of a metal-insulator-(semiconductor or semimetal) junction can yield the location in energy of conduction band edges, and locate the position of narrow conduction bands. Harrison[7] has pointed out, however, that di/dV is not expected to be simply proportional to the density of states over wide bias voltage ranges.

In the past six months, two experiments have been initiated that provide a new approach to studying tunneling into semiconductors. It is felt that these innovations are well suited to an examination of narrow bands in semiconductors, and a program is planned to apply these techniques to the study of impurity band formation in the system of antimony donors in germanium. The first innovation is to employ a superconducting metal such as lead or niobium in the junction. Below the superconducting transition temperature T_c (7.18°K for Pb, 9.34°K for Nb), singularities appear in the electron density of states of the superconductor at energies $\varepsilon_F \pm \Delta$, where ε_F is the Fermi energy, and Δ, one-half the superconducting energy gap, is (for temperatures near or below liquid helium temperature) about 1.5 milli-eV for Pb and Nb. These singularities have previously been found experimentally to be very sharp,[8] certainly narrower in energy than kT at 2°K, thereby increasing the energy resolution for tunneling from a metal in the superconducting state. In this case, direct information on the density of states is contained in the tunnel current, i, as a function of vias voltage, V. The increased resolution will be particularly important in the impurity band problem in germanium where band widths of the order of millivolts are anticipated.

The second innovation is a point contact form of tunneling junction, which has been demonstrated to be feasible by J. E. Kunzler and co-workers.[9,10] In this technique, a narrow tip having a diameter of a few microns is etched on a wire of the metal desired, an insulating oxide film is formed on the wire tip anodically,[11] and the junction (immersed in liquid helium) is formed by mechanically suspending the wire tip in delicate contact with a clean surface of the semiconductor or semimetal to be studied. This method is potentially of great advantage in the present case, since no insulating oxide is required on the semiconductor to be studied. Thus, the investigations are not limited to materials on which thermal oxidation leaves a perfect insulating film. The formation of anodic oxide films on suitable metals such as niobium and tantalum has been studied extensively and is a simple operation.

In the past six months tunneling, di/dV, measurements have been made on a degenerate p-type 0.001 ohm-cm silicon single crystal in the liquid helium temperature range, using both evaporated lead film junctions and niobium point-contact junctions. In both cases, the junctions were made to [111] silicon faces cleaved in air. Differential conductance data for low bias voltage are shown in Figures 5 and 6 for a lead film and a niobium point-contact junction, respectively. These curves are qualitatively similar to di/dV curves which are obtained in electron tunneling between a superconductor and a normal metal. The lead film junction was measured at temperatures near the critical temperature 7.18°K of lead and it was verified that the structure disappears within 0.1°K of the correct critical temperature. It was also possible to quench the superconducting properties with a dc magnetic field. The data in Figure 6 were compared with the di/dV predicted by the BCS density of states[8] for a superconductor-normal metal junction, yielding a value of the energy gap in the Nb tip within 10% of the accepted value.

It is thought that the behavior at millivolt biases arises from electron tunneling from the superconductor into an impurity band which has merged with the valence band of the silicon and which is considerably broader than the superconducting energy gap 2Δ. Although the curves shown do not contain much information on the semiconductor density of states, they demonstrate that the direct electron tunneling current at 4°K can be an easily measurable quantity, and suggest that the additional resolution inherent in the superconductor-insulator-semiconductor configuration will be realized. It is believed that the main question remaining to be answered is whether the surface barrier layer under the metal contact will remain sufficiently thin to permit a measurable tunnel current to flow in materials having a lower impurity level. Various other aspects of the di/dV data, particularly at larger bias voltages, are at present not reproducible and not fully understood.

Effort at present is being devoted to refining the point contact tunneling technique. The mechanical suspension system employed involves watch-jewel bearings and a hairspring to control the force (in the milligram range) applied to the point. The points themselves are being studied by optical and electron microscopy, and an effort is being made to fabricate points of single crystal zone refined niobium. Tunneling measurements from the tips to well-studied metals are planned to check that the point-contact data agree with data obtained from evaporated film junctions. Finally, measurements are planned using both techniques on semiconductors having lower dopings in the impurity conduction range.

Thermal Stability of Irradiation Induced Defects

The study of the thermal stability of irradiation induced defects in n-type germanium has been completed. A paper describing this work has been submitted for publication. A copy of it is attached to this report.

International Conference on the Physics of Semiconductors

Attached to this report is a copy of the manuscript that will appear in the proceedings of the International Conference on the Physics of Semiconductors to be held in Kyoto, Japan in September, 1966.

Personnel

Dr. E. L. Wolf, Mr. Ralph Hewes and Mr. Robert Spry were employed on this project during the past six months.

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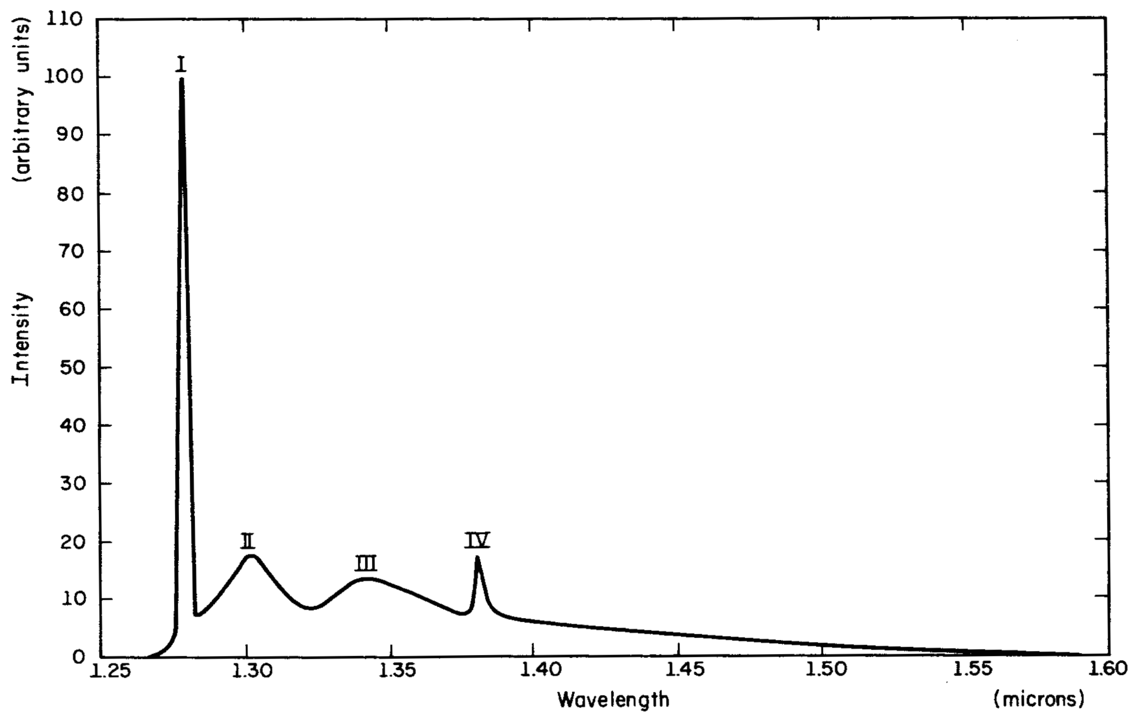

Figure 1. Recombination luminescence at liquid helium temperature from Co^{60} irradiated n-type float zone silicon 70 ohm-cm. Slit width of 1.0 mm giving a resolution of about 32 Å. Data are uncorrected for detector and monochromator response.

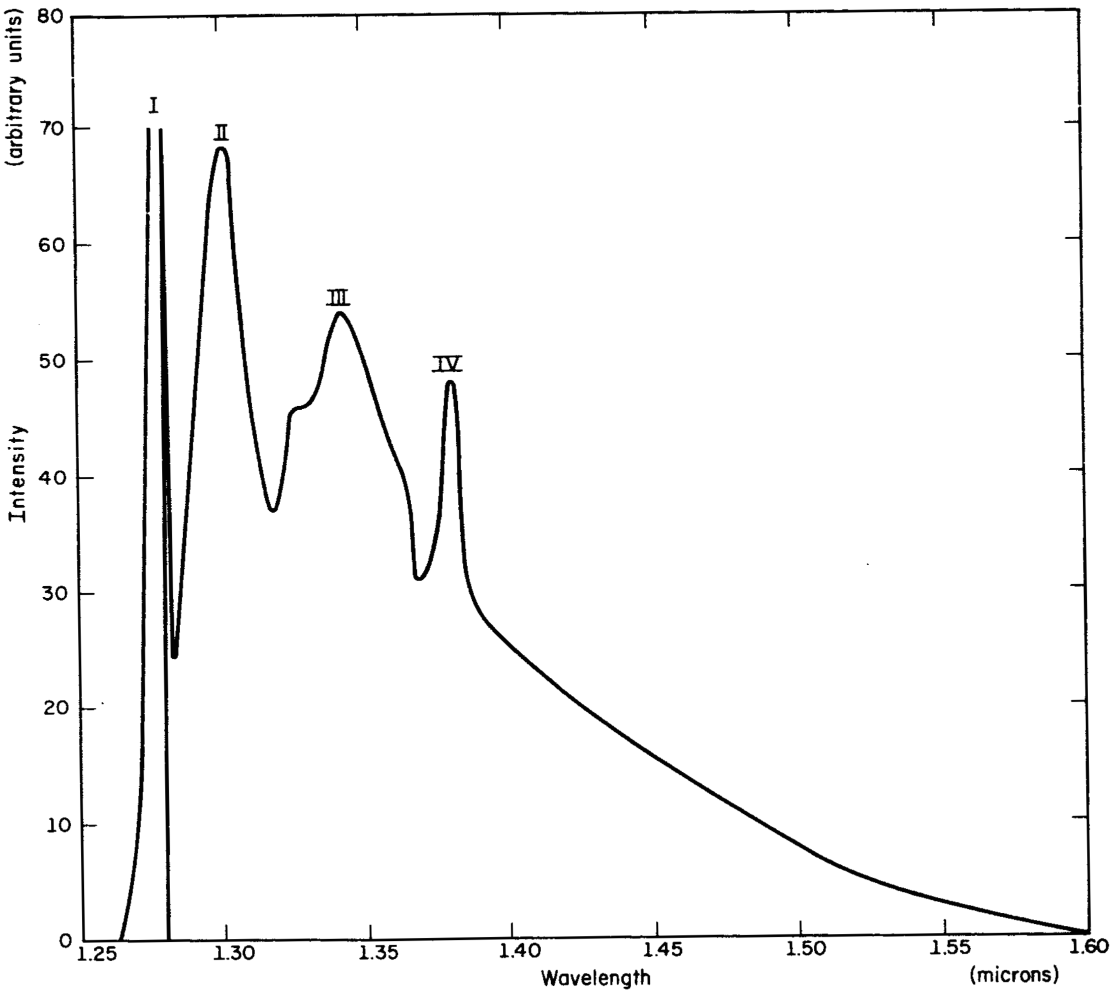

Figure 2. Recombination luminescence at liquid helium temperature from sample as in Figure 1 but at higher gain and lower resolution. Data are uncorrected for detector and monochromator response.

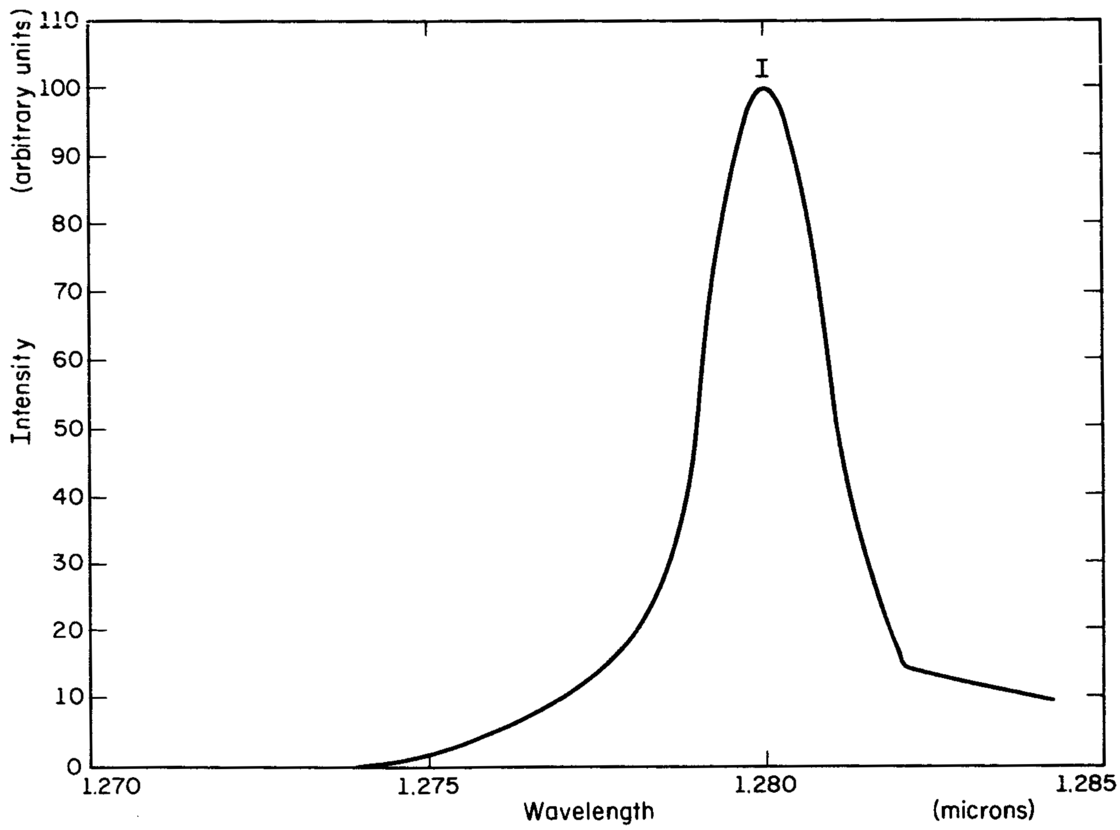

Figure 3. Recombination luminescence spectrum of narrow line centered at 1.280 microns of same sample as in Figures 1 and 2. Liquid helium temperature resolution about 16 Å. Data are uncorrected for detector and monochromator response.

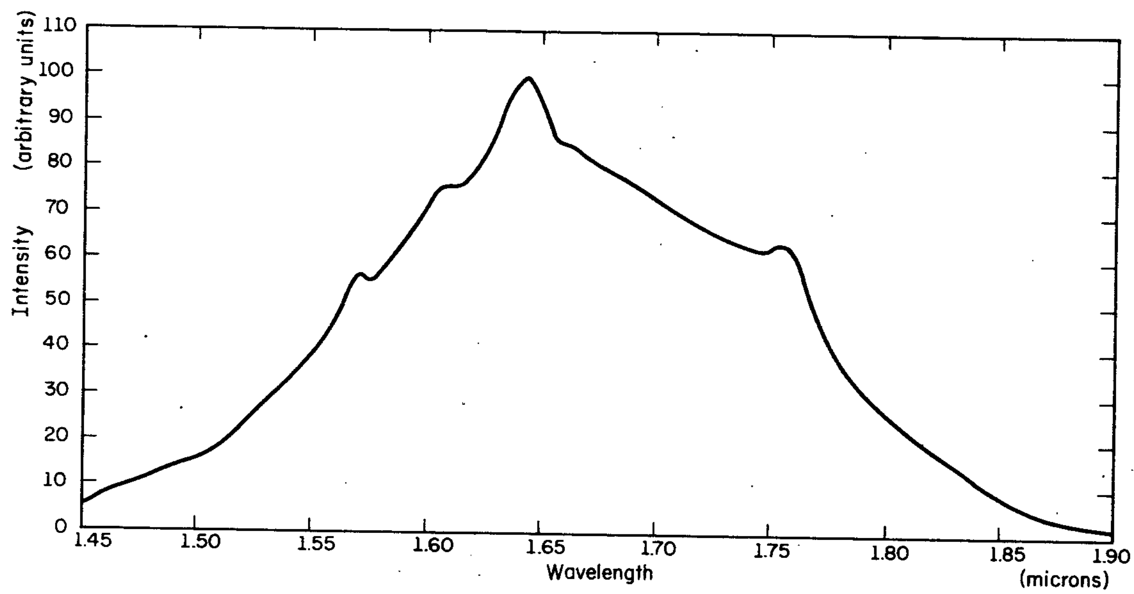

Figure 4. Recombination luminescence at liquid helium temperature from Co^{60} irradiated p-type Czochralski grown silicon 200 ohm-cm. Resolution about 32 Å. Data are uncorrected for detector and monochromator response.

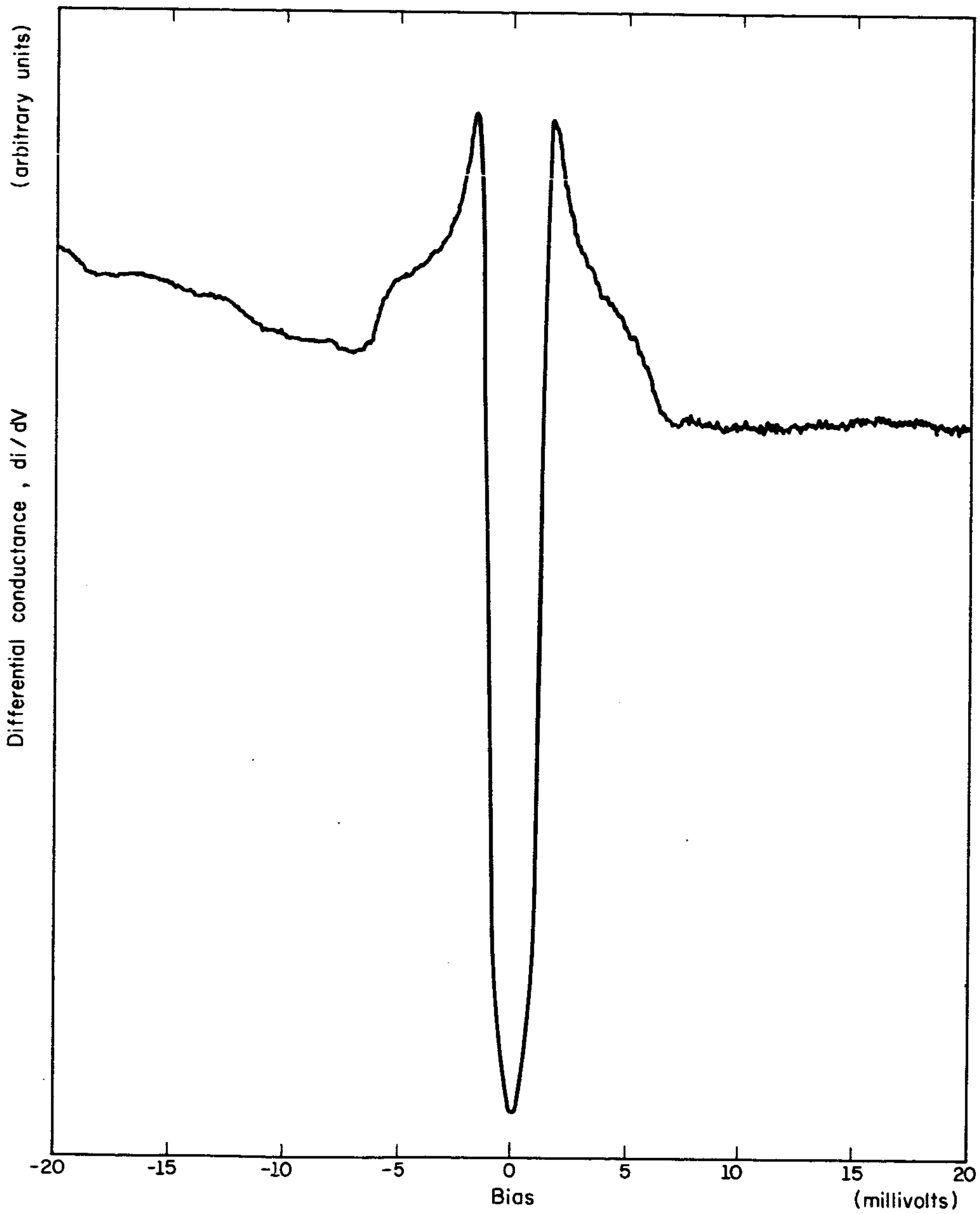

Figure 5. Differential conductance di/dV of evaporated lead film junction on p-type 0.001 ohm-cm silicon [111] cleaved surface at about 1.6°K. The oxide barrier was formed by heating the cleaved silicon to 600°C for about 10 minutes in one atmosphere of oxygen.

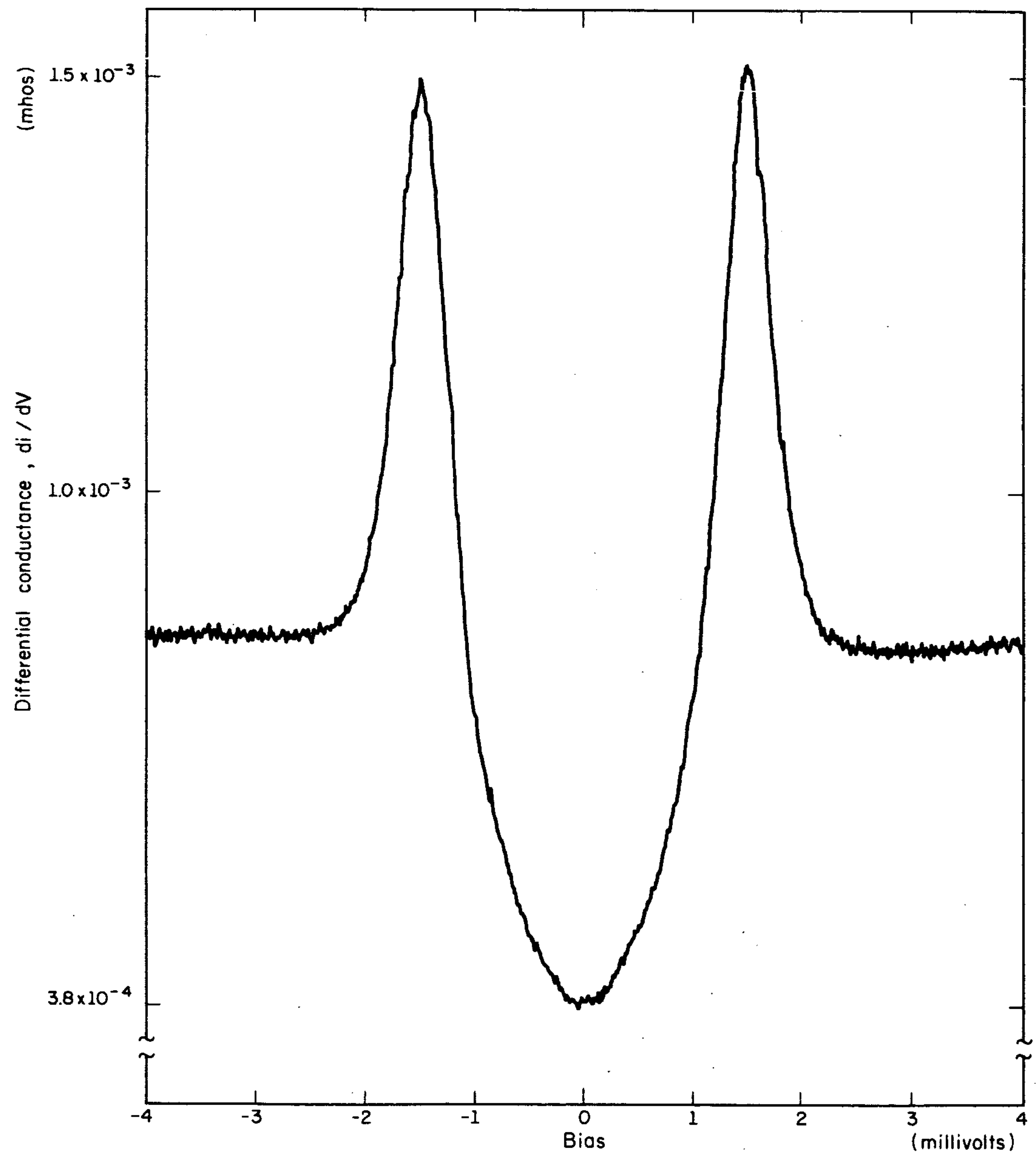

Figure 6. Differential conductance di/dV for millivolt biases of niobium point contact to 0.001 ohm-cm p-type silicon at a temperature near 1.5°K.